Multi-element background for trace elements and radionuclides in soil from Minas Gerais State, Brazil

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Abstract
Preliminary results of a multi-element geochemical background study in soils from Minas Gerais state, Brazil, are presented. Natural soils without apparent anthropogenic influence were collected to determine the content of trace elements and radionuclides in order to establish their reference values (RV). From the data analysed so far, the content of B, Ba, Cd, Co, Cr, Cu, Mn, Ni, V, and Zn presented a wide variation mirroring the diversity of parent materials. By calculating the 75 percentile (P-75) of the data distribution we observed that our results were higher than the data reported in the literature. Differences between analytical methods and the great variability of tropical soils seem to be the main restriction when the data are compared. Determining RV for trace element and radionuclides, on a regional scale, considering just descriptive statistical data, such as mean or the upper quarter (P-75) may not be realistic due to the great diversity of tropical soils. Hence correlations between trace element and radionuclides data and some soil variables are warranted to better estimate the RV for such soils.

Key Words
Toxic elements, Regulations, Contamination, Reference values

Introduction

The state of Minas Gerais, in Brazil, is a well known mineral province, where, in the past, mining activities preceded modern environmental concern and concepts. Consequently, contaminated lands presenting high trace element contents became one of the main legacies of such activities. Nowadays, the intense industrial growth, the current land-use practices, the predominance of urbanization along with the increasing demand for alternative source of energy have caused an unprecedented environmental pressure on the natural resources. Soils have particularly been at risk and possibly endangering the resilience of the ecosystems. As a general observation, natural anomalies associated with high trace elements and radionuclides contents are rather common and supplant the anthropogenic ones. In addition, natural and anthropogenic processes play a key role on the global geochemistry of those elements in soils, waters and sediments. As a result, characterization of these elements provides an important environmental index, as yet little explored in tropical soils.

The knowledge of natural concentration of trace elements and radionuclides in soils without human influence is necessary for assessing the degree of metal pollution affected by anthropogenic activities and inputs (Rojo *et al.* 2004) and before a soil to be declared contaminated. Although incipient in Brazil, the assessment of reference value (RV) is well established in many countries, i.e. United States, Germany, France and the Netherlands. The later was the foremost to publish the RV for trace elements in soils and nowadays presents a rather consolidated method for risk assessment named C-soil.

Distinct parent materials give rise to differences in the distribution of trace elements and radionuclides in soils. Thus important variations can be expected in their contents even in relatively homogeneous soil classes according to pedogenetic standards. Tropical soils, on the other hand, are subject of intense redistribution processes not only along the soil profile, but also laterally that may modify the original geochemical heritage standard. As a result, experimental studies, considering sampling under a wide range of soil types or parent materials, are warranted to elucidate the pedologic standard for distribution of trace elements and radionuclides. The purpose of this paper is to present preliminary results of a multi-element geochemical background study, in natural soils from Minas Gerais state, as a basis to estimate RV for trace elements and radionuclides at a regional level. It is a result of a cooperative project between Universities at the State of Minas Gerais and its Environmental Agency (FEAM).

Materials and methods

Study area

Located in the southeastern of Brazil, Minas Gerais is the second most populous and fourth largest State in the federation, comprising an area of about 588.384 km^2. Because it is placed in the inter-tropical zone, the pedologic mantle is mostly composed by well developed soils, such as Latosols (Ferralsols), Argisols (Acrisols), and Nitosols (Nitisols). Kaolinite in associations with iron (hydr)oxides and gibbsite is the dominant clay mineral in those soils (Fontes and Weed 1991). Cambisols occurs to a lesser extent and usually presents latosolic mineralogy.

Sampling and determination of RV

Natural soils without apparent anthropogenic influence were collected to determine the RV of trace metal and radionuclides. A total of 270 single samples were taken from undisturbed representative sites and georeferenced by Global Position System (GPS) in order to cover all the soil types (Figure 1). Each site was sampled on an area of at least 1,000 m^2 (mostly ca. 10,000 m^2) and was situated at a minimum distance of 100 m away from nearby roads. Samples were collected at 0-20 cm depth by manually driven stainless-steel auger. The material was placed into pre-labelled polyethylene bags, after removing larger stones and roots material. Prior to chemical and physical analyses, the samples were air-dried and passed through a 2-mm stainless-steel sieve to obtain the fine earth fraction (< 2 mm). A portion of 10 cm^3 of fine earth was ground in agate mortars to a grain size < 75 µm (200 meshes). Care was taken in sampling, preparation and storage to avoid accidental trace metal contamination. Prior to chemical analysis, the samples were dried at 40 ^{o}C for 48 h. Aluminium, Ag, As, B, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Se, Sb, Sr, Ti, V, W, and Zn were determined by ICP-OES and HG-ICPOES (Perkin Elmer, 3300DV). The alpha and beta total activity were determined by gamma spectrometry and the content of Th and U by ultraviolet-visible spectroscopy, following microwave extraction methods according to the standard digestion methods proposed by USEPA. Analytical quality was verified using standard reference materials NIST-SRM 2709, 2710, and 2711 for soil and IAEA 433 for radionuclides. All determination was carried out in triplicates.

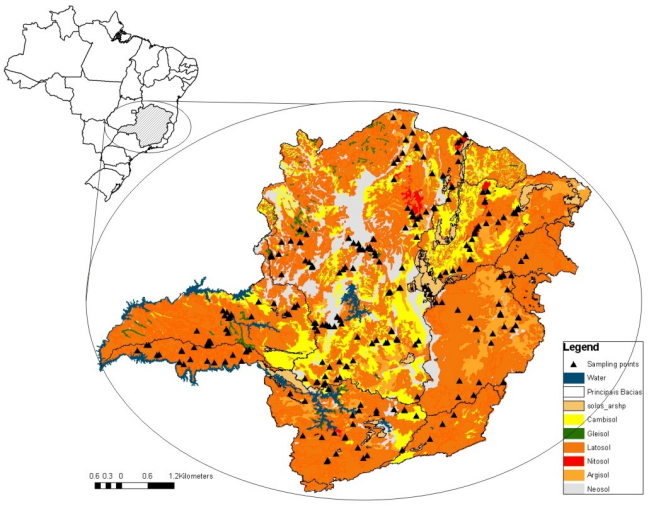

Figure 1. Sampling sites (black triangles) in Minas Gerais State covering different soil types.

Results and discussion

The recovery of elements in standard reference material SRM 2709, 2710, and 2711 were in the range of 80 – 120% of the total certified content. Preliminary results for 190 samples, randomly distributed in the Minas Gerais states, are shown in Table 1. About 80% of the total samples corresponded to soil classes of major occurrence in the state being 104 Latosols, 29 Argisols, and 19 Cambisols. Differences in the parent materials had a remarkable influence in the content of B, Ba, Cd, Co, Cr, Cu, Mn, Ni, V, and Zn where the values presented a wide variation. Except for B the average content of the other elements were lower than those reported by Marques *et al.* (2004) for soils from the Cerrado region in Minas Gerais. Such pattern was already expected as we used the USEPA 3051a leaching method, which does not achieve a complete extraction of the analyte from the sample. A very noticeable B anomaly appears as compared with both, the world soil and Paraná soil averages as reported by Kabata-Pendias and Pendias (2001) and Licht *et al.* (2006), respectively.

Table 1. Trace elements descriptive statistics in soil samples (n = 190) in comparison with published data.

	B	*Ba*	*Cd*	*Co*	*Cr*	*Cu*	*Mn*	*Ni*	*V*	*Zn*
	---------- mg/kg----------									
Min.	3.88	1.91	< 0.02[1/]	< 0.02	1.85	< 0.02	6.99	< 0.02	< 0.02	2.17
Max	288.06	676.77	1.62	75.37	1387.35	178.64	2212.26	505.85	570.88	234.76
Mean	71.22	75.61	0.43	5.97	77.80	19.55	244.55	19.44	95.69	30.24
Med	55.88	51.53	0.36	1.88	49.04	12.59	136.24	12.37	58.22	23.46
P-75[2]/	**97.60**	**105.61**	**0.61**	**6.44**	**90.60**	**21.21**	**286.50**	**20.36**	**129.55**	**37.37**
P-90[3/]	**139.37**	**168.88**	**0.91**	**14.94**	**163.44**	**38.01**	**609.90**	**31.65**	**221.31**	**56.42**
WS[4/]	30	500		13	65	20	545	20	90	50
MG[5/]		67 ± 127		5 ± 6	112 ± 69	33 ± 55	455 ± 583	14 ± 13	257 ± 231	38 ± 54
PR[6/]	6–99 (24)	43–502 (147)			43–62 (87)	20–319 (117)	135–1980 (538)		81–856 (360)	24–124 (77)
Fadigas *et al.* (2006) P-75			0.4	2	43	2		12		12
Lemos (2000) P-75		75	< 0.5	13	40	35		13	275	60

[1]/Values followed by the < signal mean the detection limit; [2]/Upper quarter (75 percentile of the frequency distribution); [3]/90 Percentile of the frequency distribution; [4]/World Soil (Kabata-Pendias and Pendias 2001); [5/] Minas Gerais Cerrado soils (mean ± standard deviation; Marques *et al.* 2004). [6/] Paraná soils (Licht *et al.* 2006; n = 307)

Despite B being highly mobile under oxidizing and acidic conditions, its enrichment can be due to the presence of a large calcareous province in Minas Gerais. It is well known that calcareous soils often show a relatively high B enrichment, inherited mainly from parent rock material. Establishing RV for trace elements in soils is rather subjective and depends on the criteria regionally defined. Two parameters related to data distribution frequency have been used, i.e. 75 percentile (upper quarter P-75) and 90 percentile (P-90). The former is more conservative and has been preferred in environmental agencies which are concerned about the fate of the contaminants in the geoecosystem. In this work, the values corresponding to the P-75 were in general higher than the data reported by Fadigas *et al.* (2006) and Lemos (2000). By considering the similarity of soils classes used by Fadigas *et al.* (2006) such behaviour would not be expected. The results discrepancy could again be attributed to differences between analytical methods since they used aqua regia as extractor. In fact large differences between aqua regia and USEPA 3051a methods are not expected, but Campos *et al.* (2003) obtained Pb contents using the USEPA 3051a, in average, 29% higher than those reported by Pierangeli *et al.* (2001) to similar Brazilian soils, but using aqua regia as extractor. The differences can also be ascribed to the sampling method as the majority (60%) of the samples used by Fadigas *et al.* (2006) were taken from sub-soil layer (> 30 cm). Higher values of P-75 observed for Ba (105.61 mg/kg), Cd (0.61 mg/kg), Cr (90.60 mg/kg), and Ni (20.36 mg/kg) as compared to the data reported by Lemos (2000) to soils from São Paulo State are not expected. Basaltic rocks, which are naturally enriched in those trace elements, are common parent materials for soils in São Paulo. On the other hand, in Minas Gerais State the lithology is quite variable, being common soils derived from granitic rocks.

Conclusion

Determining RV for trace element and radionuclies by considering just descriptive statistic data, such as mean or upper quarter (P-75) may not be realistic due to the great diversity of tropical soils. Therefore, the correlation between the results and some soil variables is warranted to better estimate the RV.

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